Annealing Study of ALD Deposited Ferroelectric Al-doped HfO_2

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Outline

Introduction

- Background
- Previous Work at RIT
- Project Objectives

Process

- ALD Deposition
- Fabrication of Capacitors

Results

- Hysteresis Measurements
- Comparisons with Literature

Conclusion and Future Work

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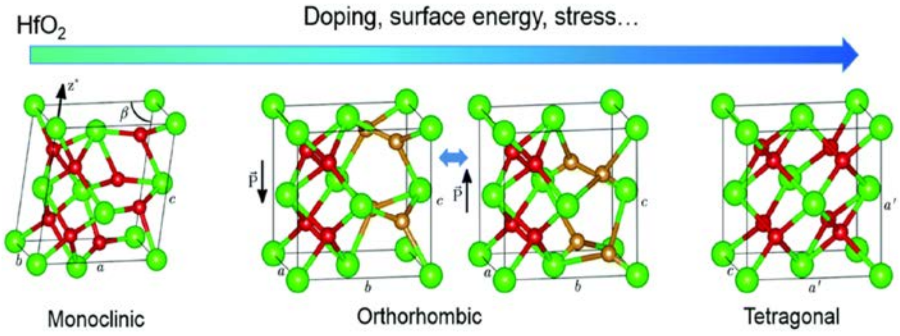
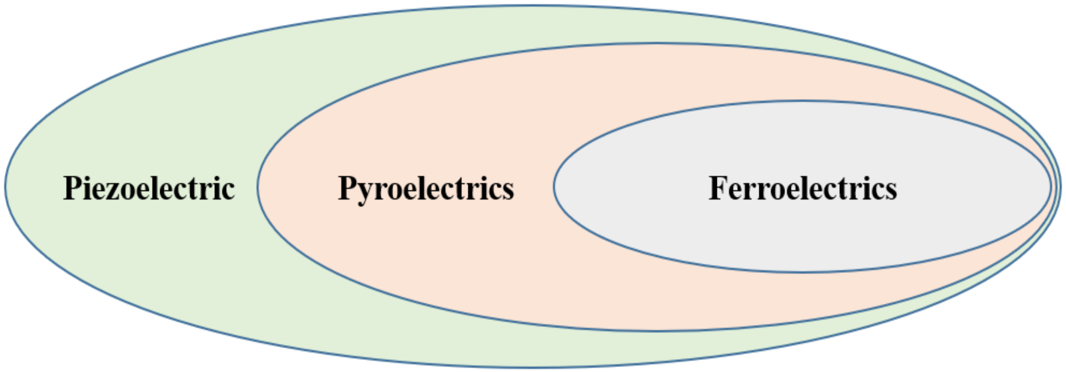
What is Ferroelectricity?



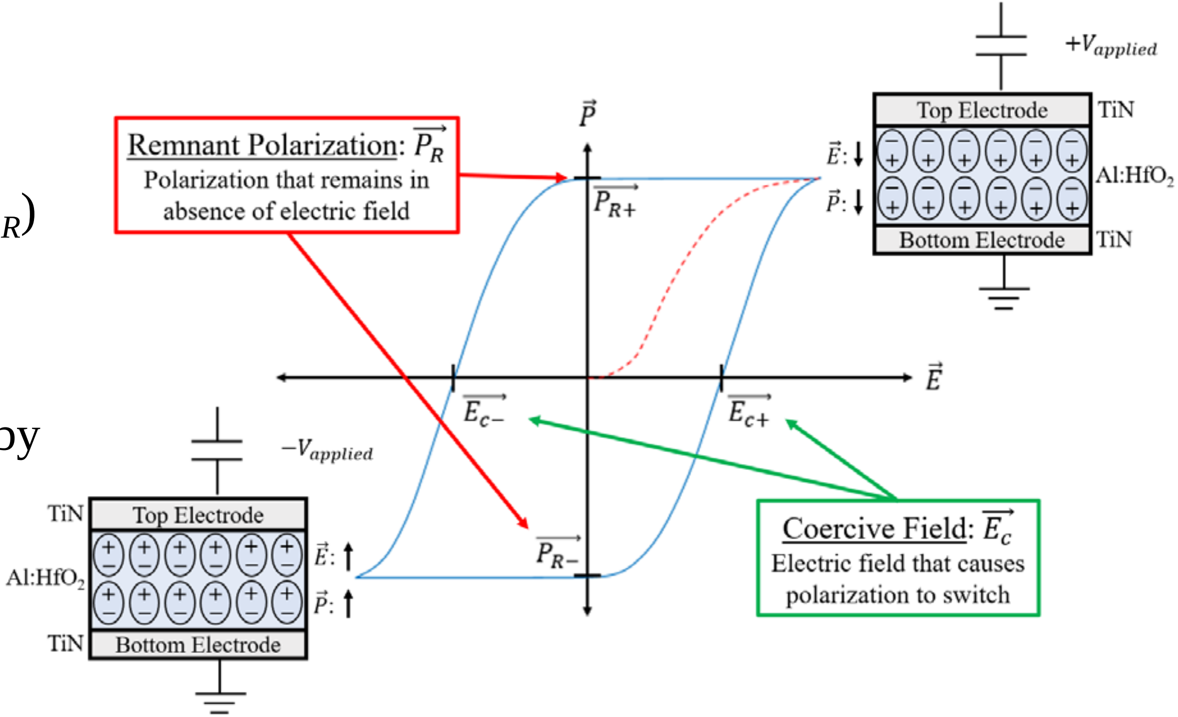


Dielectrics

- Centro-Symmetric
- Piezoelectric (Non-Centro Symmetric)
  - Non-pyroelectrics
  - Pyroelectrics
    - Non-ferroelectrics (Anti-ferroelectric)
    - **Ferroelectrics**

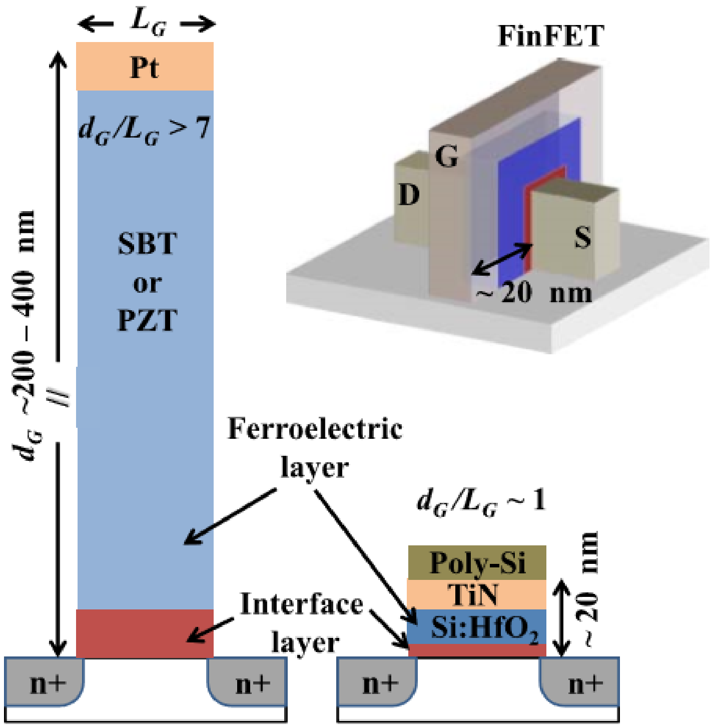
What is Ferroelectricity?

- Spontaneous polarization of dielectric film
- Retains remnant polarization (P_R) in absence of electric field
- Can retain both positive and negative P_R, which is switched by applying coercive field (E_C)
- Attractive for non-volatile memory applications



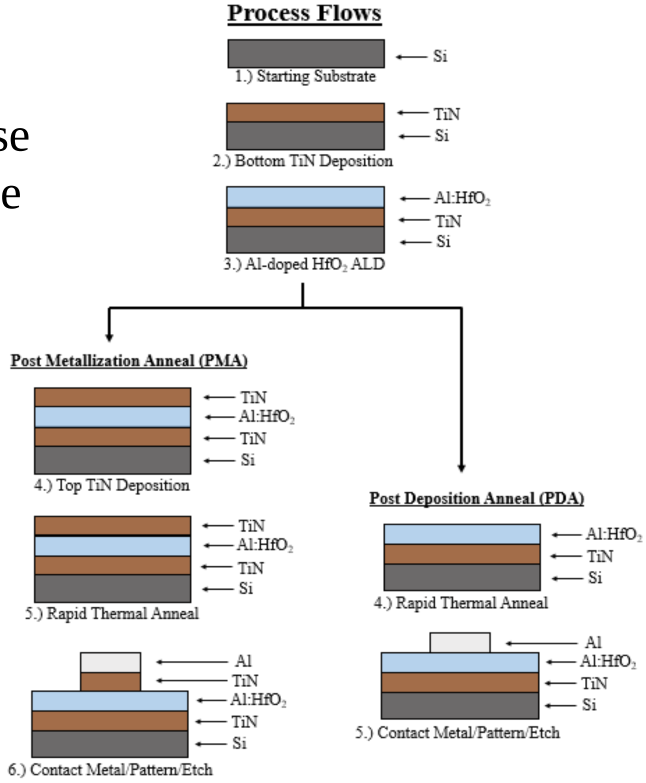
Why HfO_2?

- Traditional ferroelectric materials, such as lead zirconate titanate (PZT) or strontium bismuth tantalite (SBT), are difficult to scale with modern integrated circuits
  - Require large thickness to achieve useful ferroelectric properties
  - Also requires thick buffer layer
- HfO_2 is already widely used as a high-k dielectric in modern CMOS processes
- Can obtain relatively high E_C values at thin film thicknesses. This enables scaling of various ferroelectric memory devices



Post-Metallization vs. Post-Deposition Annealing

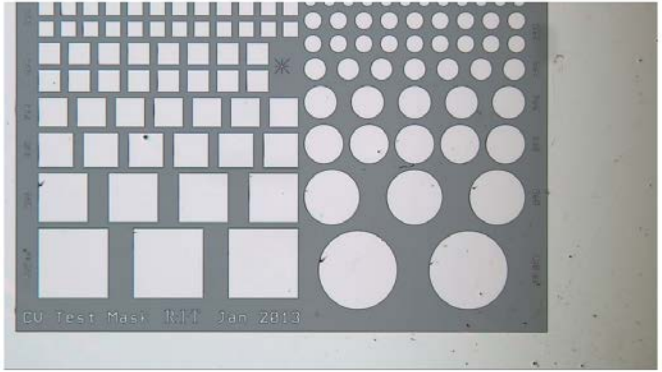
- Generally require a top electrode to mechanically confine the ferroelectric layer during rapid thermal annealing (RTA). TiN is commonly used for this purpose
- Recent research has shown that it is possible to fabricate ferroelectric HfO_2 without a top TiN electrode using Aluminum (Al) as a dopant
  - Previously thought to only be possible when using Yttrium (Y) as a dopant
- Post-Metallization Annealing (PMA)
  - Annealing with a top electrode present
- Post-Deposition Annealing (PDA)
  - Annealing without a top electrode present

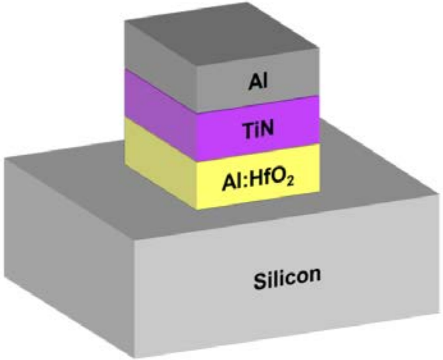


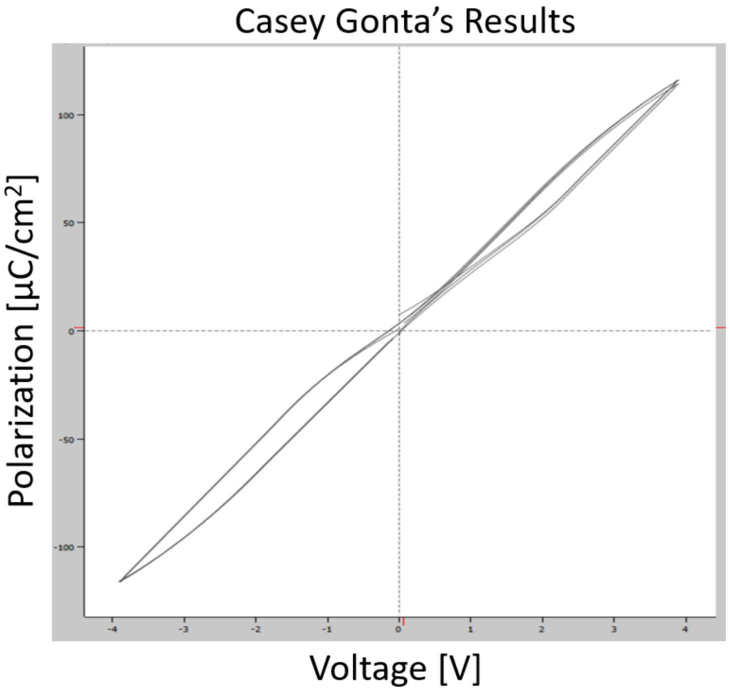
Previous Work at RIT

- Ferroelectric Capacitors using atomic layer deposition (ALD) Al-doped HfO_2 have been fabricated at RIT by Casey Gonta

- Polarization testing indicated anti-ferroelectricity in the Al:HfO_2 layer







Project Objectives

Goal: To fabricate ferroelectric Al-doped HfO_2 using atomic layer deposition at RIT

1. Develop ALD recipe for ferroelectric Al-doped HfO_2

2. Fabricate capacitors with ferroelectric Al:HfO_2 as dielectric
    a) Fabricate both PMA and PDA devices

3. Perform polarization testing on fabricated capacitors to verify ferroelectricity
    a) Compare PMA devices to PDA devices

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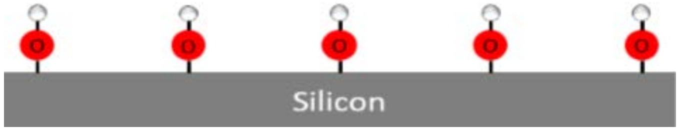
Atomic Layer Deposition of HfO_2

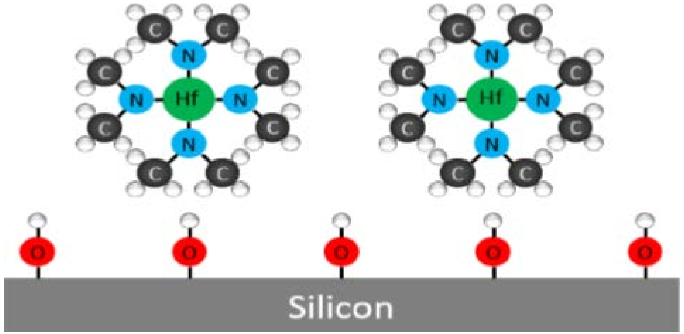
0.) Starting Substrate

- H_2O is initially pulsed, OH groups present on Si surface



1.) Introduce Hf precursor

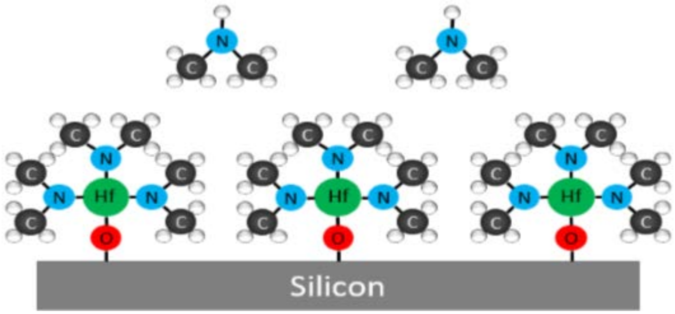
- TDMAHf - $Hf(N(CH_3)_2)_4$ Tetrakis(dimethylamido)hafnium(IV)



Atomic Layer Deposition of HfO_2

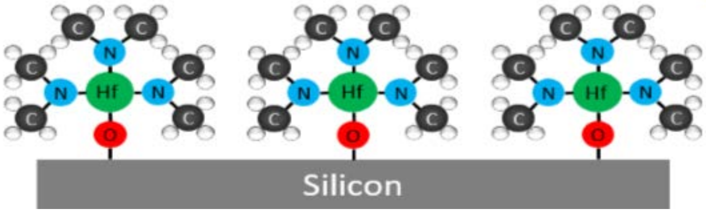
2.) Self-Limiting Surface Reactions

- TDMAHf reacts with Hydroxyl groups
- By-product: Dimethylamine $(CH_3)_2NH$



3.) Chamber Purge

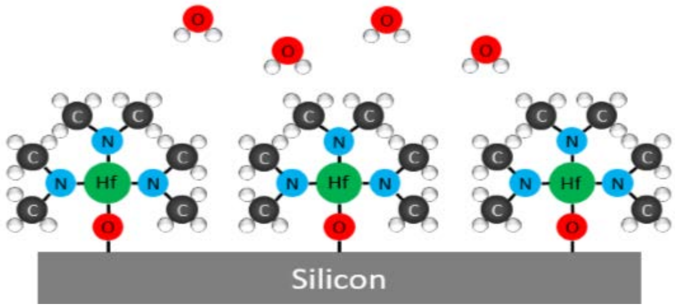
- Unreacted TDMAHf removed
- By-product Dimethylamine removed



Atomic Layer Deposition of HfO_2

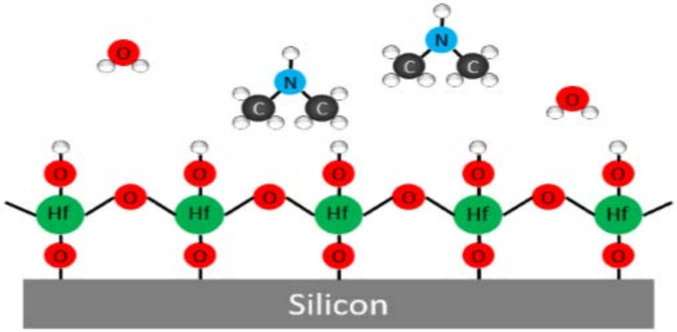
4.) H_2O Pulsed

- In order to react with dimethylamine groups on Hf atoms



5.) Surface Reactions

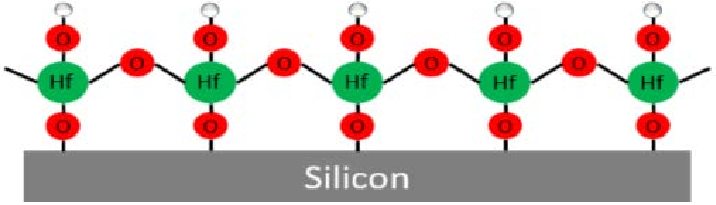
- Reaction leaves Hf-O-Hf bridges and hydroxyl groups on surface
- By-products: dimethylamine and H_2O



Atomic Layer Deposition of HfO_2

6.) Chamber Purge

- Unreacted H_2O removed
- By-product Dimethylamine removed



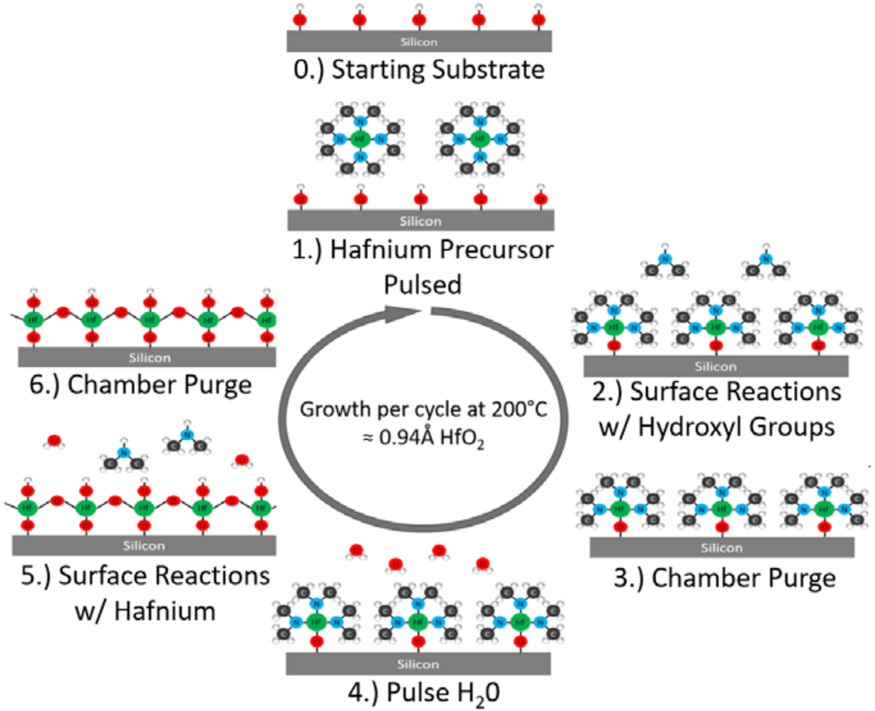
Atomic Layer Deposition of HfO_2

Repeat

- Each cycle deposits a monolayer of HfO_2 at a time
- Layer after layer is deposited to obtain HfO_2 film

Thickness Control

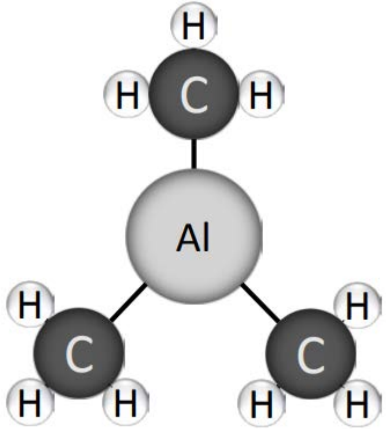
- Control thickness by number of cycles
- Growth Rate per cycle ~ 0.94Å at 200°C



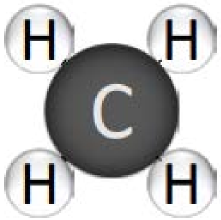
Introducing Al Dopant

- Every “x” cycles of Hf precursor, an Al precursor is pulsed to introduce into the HfO_2 film
- The number of “x” Hf precursor cycles in between Al cycles is what determines the concentration of Al dopant in the HfO_2 film
- Al precursor: TMA – Trimethyl aluminum
- By-product of reaction with hydroxyl group and H_2O is methane, CH_4

Al Precursor: TMA

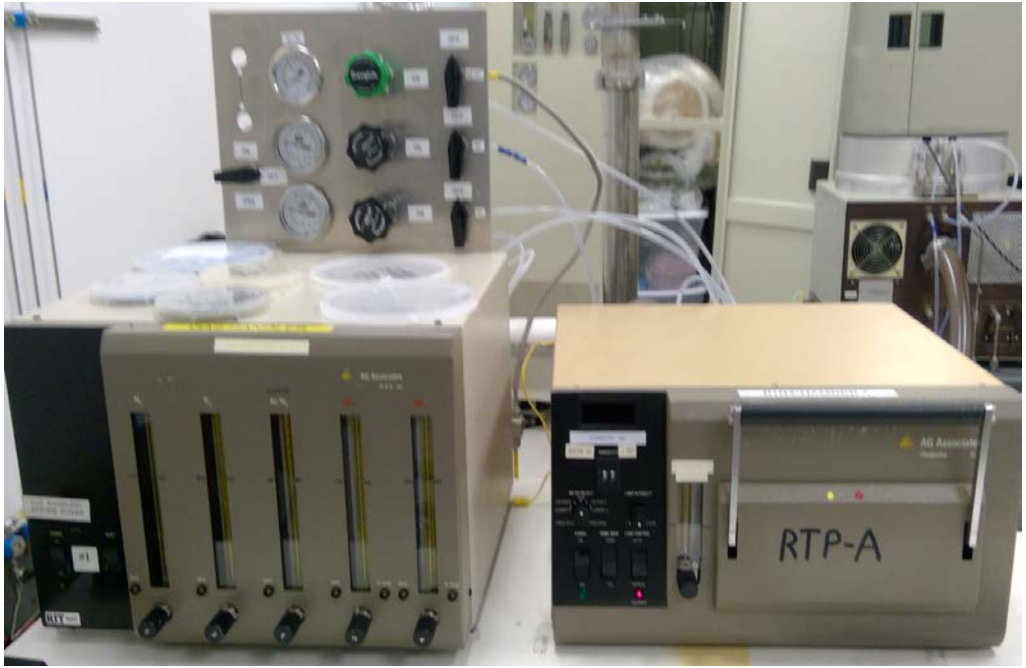


By-product: Methane



Savannah ALD and RTP Tools Used

Ultratech Savannah ALD

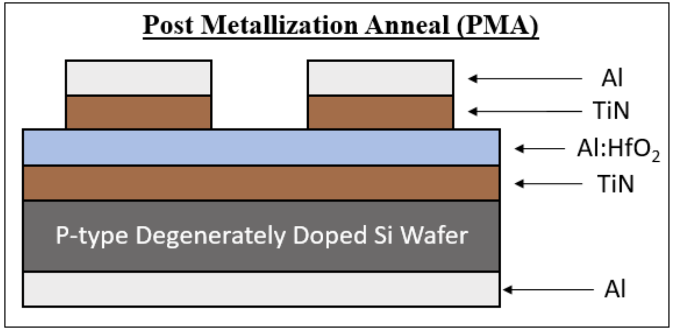


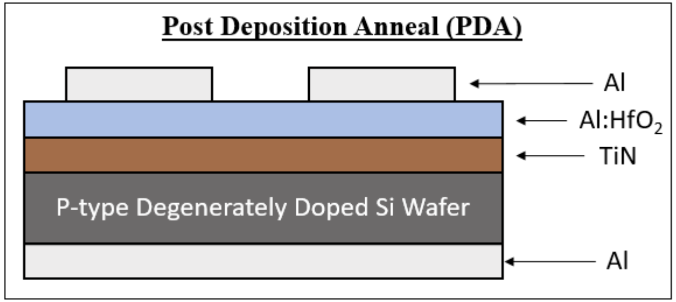
AG610A Rapid Thermal Processor

Fabrication of Capacitors

- Capacitors were fabricated using both PMA and PDA process flows
- Investigated effects of annealing temperature and time, as well as Al dopant concentration in the HfO_2 film

Sample	Process	Al Percentage	RTA Temp [°C]	RTA Time [s]
1	PMA	3.03%	800	60
2	PMA	3.03%	1000	30
3	PDA	3.03%	1000	30
4	PMA	2.70%	1000	60
5	PDA	2.70%	1000	60





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Polarization Measurement Systems

Polarization measurements taken at RIT using aixACT TF Analyzer 1000

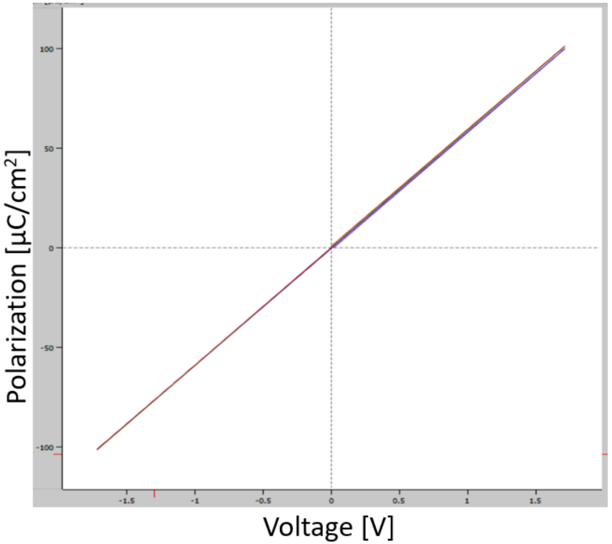
Test Setup

aixACT TF Analyzer 1000

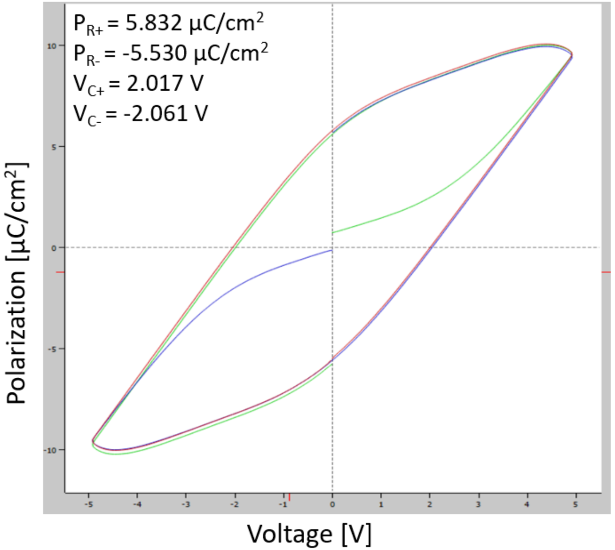
Hysteresis Measurements

Ferroelectricity observed in both PDA samples; Not observed in PMA Samples

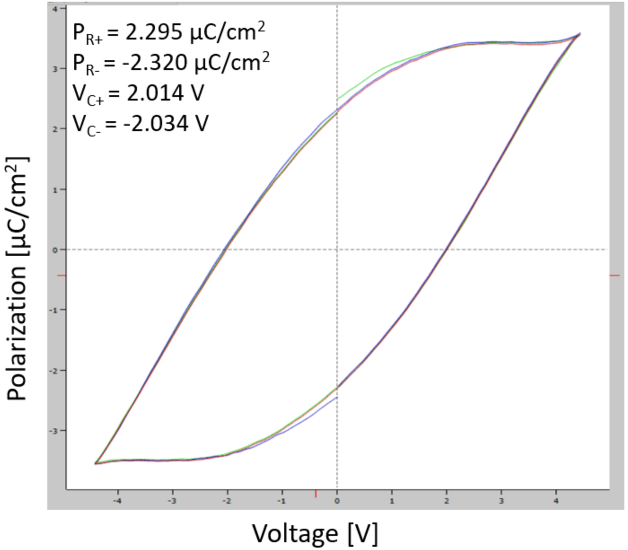
PMA – 3.03% Al, 1000°C 60 second RTA



PDA – 2.70% Al, 1000°C 60 second RTA



PDA – 3.03% Al, 1000°C 30 second RTA



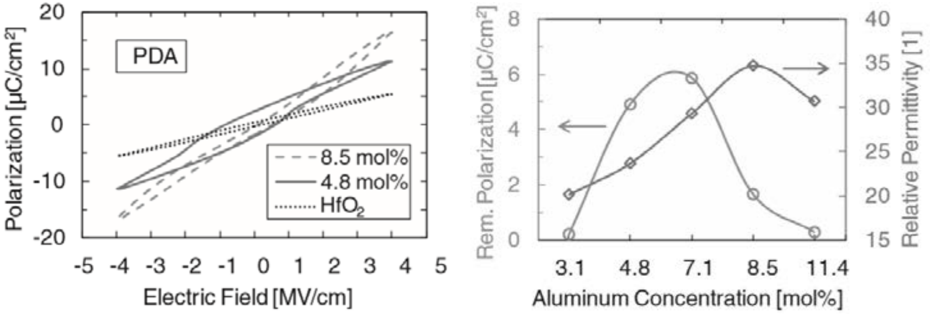
Capacitor characteristics observed in PMA devices

Comparison with Literature

Results obtained at RIT are comparable with literature

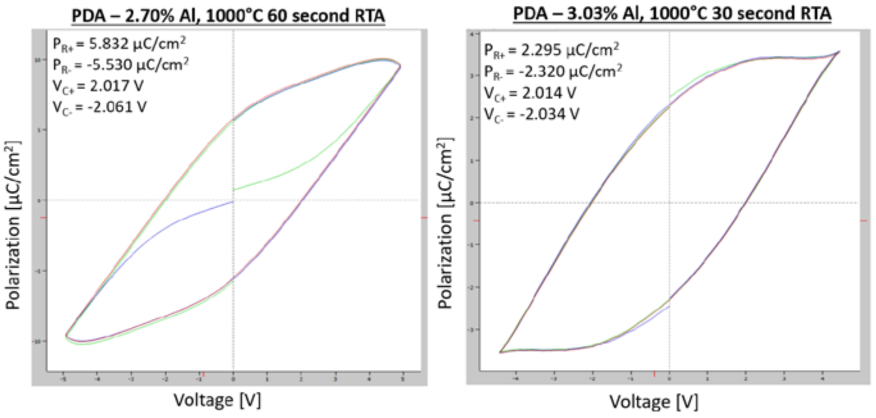
- 2.70% Al concentration capacitors at RIT and 4.8% Al concentration capacitors from literature have similar P_R values
- Need to verify Al concentration via XRD measurements

Literature



16nm Al:HfO_2 Samples
1000°C, 20 second Anneal

RIT Results



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Conclusions

- Ferroelectric Al:HfO_2 capacitors were fabricated at RIT using ALD
- Ferroelectricity was observed in PDA fabricated devices
- Ferroelectricity not observed in PMA fabricated devices, likely due to imperfect top TiN layer
- Observed higher remnant polarization values with longer annealing times on samples with same annealing temperature
- Comparison with literature indicates similar remnant polarization (P_R) values

Future Work

- Optimization of top TiN electrode
- Optimization of ALD and annealing recipes for ferroelectric Al:HfO_2
- Characterization of *n* and *k* values for ferroelectric Al:HfO_2
- Thickness study of ferroelectric Al:HfO_2
- Development and characterization of Al:HfO_2 etching technique
- Fabrication of ferroelectric devices solely at RIT
    - Ferroelectric Tunnel Junctions (FTJ)
    - Ferroelectric Field Effect Transistors (FeFET)
    - Negative Capacitance Field Effect Transistors (NC FET)

Acknowledgements

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Thank You!